# CHEMICAL CHANGES INDUCED BY IRRADIATION IN MEATS AND MEAT COMPONENTS

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**Abstract — Résumé — Аннотация — Resumen**

CHEMICAL CHANGES INDUCED BY IRRADIATION IN MEATS AND MEAT COMPONENTS. The acceptability of meats preserved by irradiation has been hampered by the formation of an irradiation flavour and odour. This flavour and odour is believed to be due to the volatile chemical compounds produced by radiation impact on the protein and lipid molecules.

The analysis of the volatile compounds has been accomplished, employing programmed cryogenic temperature gas chromatography for separation of the complex mixtures obtained, and rapid scanning mass spectrometry for identification of the individually separated components. Comprehensive analyses of the volatiles from irradiated ground beef, pork, mutton, lamb, and veal, as well as the volatile irradiation degradation products of several amino acids and proteins, animal fats, methyl esters of fatty acids, and triglycerides have been made.

The results of the analysis of the irradiated component meat substances are compared with those obtained from the irradiation of meat itself, and of separate meat fractions, thus establishing the contribution of each fraction to the total. Mechanisms are postulated for the formation of the volatile components from each fraction and for interactions among intermediates from different fractions.

TRANSFORMATIONS CHIMIQUES PROVOQUEES PAR LES RAYONNEMENTS DANS LES VIANDES ET LEURS CONSTITUANTS. La comestibilité des viandes conservées par les rayonnements s'est trouvée diminuée à la suite de l'apparition dans celles-ci d'un goût et d'une odeur engendrés par l'irradiation. On pense que ces derniers sont dus aux composés chimiques volatils qui sont formés par l'action des rayonnements sur les molécules des protéines et des lipides.

Il a été procédé à l'analyse des composés volatils à l'aide d'un programme de chromatographie en phase gazeuse à température cryogénique visant à séparer les constituants des mélanges complexes obtenus, et par spectrométrie de masse à balayage rapide destinée à identifier les constituants séparés. L'auteur a effectué des analyses complètes des composés volatils émanant de viande hachée de bœuf, de porc, de mouton, d'agneau et de veau; il a également analysé les produits volatils de la dégradation, par les rayonnements de plusieurs acides aminés et protéines, de graisses animales, d'esters méthyliques d'acide gras et de triglycérides.

L'auteur compare les résultats de l'analyse des substances constitutives de la viande soumises à l'irradiation avec ceux obtenus par l'irradiation de la viande elle-même et de fractions distinctes de viande, ce qui permet de déterminer l'apport de chaque fraction à l'ensemble. Il postule des mécanismes expliquant la formation des éléments volatils dans chacune de ces fractions ainsi que les interactions entre les substances intermédiaires des différentes fractions.

ХИМИЧЕСКИЕ ПРЕВРАЩЕНИЯ В МЯСНЫХ ПРОДУКТАХ И ИХ СОСТАВНЫХ ЧАСТЯХ ПОД ВОЗДЕЙСТВИЕМ ОБЛУЧЕНИЯ. Облучение различных сортов мяса с целью консервации отражается на вкусовых качествах, вызывая появление специфического привкуса и запаха. Полагают, что это объясняется образованием летучих химических соединений при действии радиации на белки и липидные молекулы.

Анализ летучих соединений осуществляется на газовом хроматографе с криогенным охлаждением до заданной температуры, где происходит разделение сложных смесей. Идентификация выделенных компонентов проводится с помощью масс-спектрометрии с быстрым скеннированием. Проведен исчерпывающий анализ летучих соединений, выделяющихся из говядины, свинины, баранины и телятины, которые были облучены, а также анализ летучих соединений, образующихся при разложении под действием облучения некоторых аминокислот, белков, животного жира, метиловых эфиров жирных кислот и триглицеридов.

Результаты анализов облученных компонентов мясных продуктов сравниваются с результатами, полученными при облучении самого мяса и его отдельных фракций, что дает возможность установить роль каждой фракции в целом. Постулируются механизмы образования

летучих компонентов от каждой фракции, а также взаимодействие промежуточных продуктов от различных фракций.

ALTERACIONES QUIMICAS PRODUCIDAS POR IRRADIACION DE LAS CARNES Y DE SUS COMPONENTES. El mal sabor y el mal olor originados por la irradiación de la carne conservada son un obstáculo para su aceptación. Se cree que este sabor y este olor desagradables se deben a los compuestos químicos volátiles producidos por las radiaciones en las moléculas de proteínas y lípidos.

Se han analizado los compuestos volátiles por cromatografía en fase gaseosa a temperaturas sumamente bajas y con arreglo a un programa, para determinar las mezclas complejas obtenidas, y por espectrometría de masas con exploración rápida, para identificar los componentes separados. Se han efectuado análisis minuciosos de las sustancias volátiles formadas por irradiación en carne picada de vaca, cerdo, carnero, cordero y ternera, así como de los productos volátiles de degradación originados por las radiaciones en varios aminoácidos y proteínas, grasas animales, ésteres metílicos de ácidos grasos y triglicéridos.

Los resultados del análisis de los componentes de la carne irradiados se comparan con los obtenidos irradiando la carne misma y distintas fracciones de ella. Se postulan los mecanismos de formación de los componentes volátiles de cada fracción y los de las interacciones de las fases intermedias correspondientes a distintas fracciones.

The acceptability of meats preserved by irradiation has been hampered by the formation of an irradiation flavour and odour. Studies of this problem have been in progress in many laboratories for several years in order to discover the nature of the irradiation flavour and how to prevent it. This flavour and odour is believed to be due to the volatile chemical compounds produced by radiation impact on the protein and lipid molecules, and it has been a basic assumption that chemical analysis would show by comparison of irradiated with unirradiated meat that certain compounds might be responsible for the undesirable effects. The objective of the studies of chemical changes induced by irradiation is to discover the precursors of the volatile compounds and the mechanisms by which they are formed.

There are three sensory observations related to the production of irradiation odour which have influenced the choice of irradiation conditions and technique, and which all serve to delineate the problem more clearly. Firstly, irradiation odour in raw meat is a characteristic property, is the same for beef, pork, lamb, and the other meats, and does not vary in type but only in intensity. Secondly, the odour is reproducible, and given radiation doses can produce approximately the same odour. Thirdly, irradiation odour is the direct result of changes due to irradiation impact, and does not depend on the type of irradiation employed, nor on the presence of such variables as water or oxygen in the surrounding environment.

In this paper the author describes the principal facts relating to the analytical composition of volatile compounds produced in irradiated meat, and of a number of model systems, in the hope that this information will provide some understanding of the mechanism of the formation of such compounds.

During the past decade several groups of investigators [1-10] have contributed to the identification of some of the volatile compounds isolated from irradiated meats. They have established the presence of several types of compounds, including carbonyls, alcohols, thiols, thioalkanes and esters, and have demonstrated a quantitative relationship between the presence of these compounds and the irradiation dose. They have shown that, as the dose increases, the amounts of the various oxygenated and sulphurated compounds increase. However, all the compounds have been found to be present in unirradiated meat, and their presence in greater amount in the irradiated product may contribute to the overall flavour, but their presence from the viewpoint of chemical composition is not peculiar to irradiated meat. Recent work [11-13] has shown, through the use of new analytical techniques, that homologous series of n-alkanes and n-alk-1-enes can be found in irradiated ground beef, and that these hydrocarbons are not found in appreciable amounts in an unirradiated control sample. These results are discussed in detail below.

## EXPERIMENTAL

The preparation of the samples of irradiated ground beef and the isolation and collection of the volatile components were accomplished by procedures already described [5, 12, 14]. The total condensate was collected by high vacuum distillation at room temperature and then further separated into a "water fraction" and a "carbon dioxide" fraction by vacuum distillation at −80°C. The components of the carbon dioxide fraction were separated by a cryogenically-programmed temperature gas chromatograph and identified in the eluate by means of a rapid-scanning mass spectrometer. The components of the water fraction were also identified by means of the combined gas chromatograph-mass spectrometer after extraction with ether. The details of the analytical procedures are described in previous publications [5, 12, 14-17].

Table I summarizes the various meats, meat constituents and other related substances that were analysed. The substances chosen were intended to provide a cross-section of the type of inherently related material from which volatile odour and flavour compounds might be expected to form. Thus, in addition to several whole meats, the volatile irradiation products from a number of protein and lipid substances were also analysed. Among the lipid substances were included typical whole fats and separate moieties, such as triglycerides, fatty acid esters, and cholesterol, as an example of a steroid. Among the proteinaceous substances were included a protein, a polypeptide and some individual amino acids. Finally, beef itself was separated into a protein, a lipid and a lipoprotein fraction and these were irradiated and analysed.

## RESULTS AND DISCUSSIONS

The formation of volatile compounds in beef is a reproducible phenomenon. Figure 1 shows two cryogenically-programmed gas chromatograms of a carbon dioxide fraction of irradiated ground beef volatiles isolated from two separate samples of meat, one irradiated in February 1960, the other in November 1960. The amount of sample and temperature programme rates were slightly different in each case, but the overall similarity of the sample composition is readily apparent.

Although beef has been studied extensively, very few, if any, significant analyses of other meats have been performed until recently [12]. A comprehensive analysis of the volatiles from irradiated ground beef, pork, mutton, lamb and veal showed that the compounds formed are

TABLE I. SUBSTANCES EMPLOYED FOR IRRADIATION STUDIES

| Whole Meats | Lipid | Protein |
|---|---|---|
| Beef | Beef fat | Haddock (0.3% fat) |
| Veal | Butterfat | Beef protein |
| Mutton | Triglycerides | Oxytocin |
| Lamb | Fatty acid esters | Amino acids |
| Pork | | |
| | Cholesterol | |
| | | Beef lipoprotein |

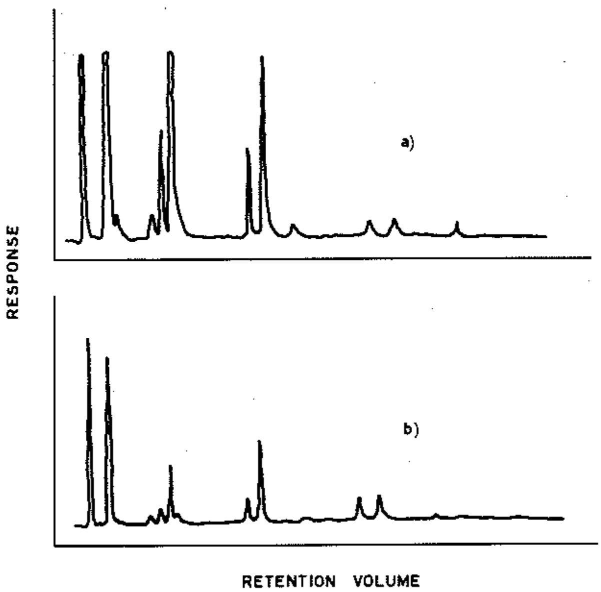


FIG. 1. Gas chromatograms of irradiated beef volatiles, a) Irradiated February 1960, b) Irradiated November 1960

essentially the same in all the meats. All the samples were irradiated at a dose of 6 Mrad and the complete analyses of the volatiles produced show the presence of more than 80 compounds, many in appreciable quantity. The controls, or unirradiated samples, showed the presence of only trace quantities of compounds, except for expected components, such as ethanol, acetaldehyde or acetone. The compounds identified are too numerous to tabulate here, but complete tabulations may be readily found in the literature [12, 17, 18].

The most abundant components were the hydrocarbons. Figure 2 shows the distribution of n-alkanes found in a sample of irradiated beef

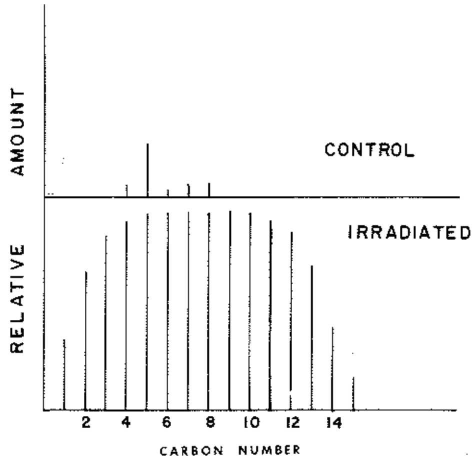


FIG. 2. n-Alkanes identified in the volatile compounds isolated from irradiated beef

volatiles compared with a control. The small amounts of the hydrocarbons found in the unirradiated control are probably due to oxidation of the meat fat during storage. A similar distribution of n-alkanes was found in the volatiles from mutton, lamb, pork and veal. There were essentially no hydrocarbons in the controls. A distribution of normal alk-1-enes, corresponding to the normal alkanes but in smaller quantity, was found to exist uniformly in all the irradiated meat samples. The olefin compounds, together with the alkanes, constitute approximately 90 to 95% of the total composition of the total volatile constituents isolated. Alkanes constitute about 60% and alkenes about 40% of the total hydrocarbon content. Trace amounts of n-alkynes are also found among the hydrocarbons isolated from the various meats.

Alkanes are usually regarded by chemists as nearly odourless. Alkenes, on the other hand, and more particularly, alkynes, are definitely odorous. The unsaturated compounds cannot be disregarded as potential sources of odour and the saturated compounds may also contribute, notwithstanding previous opinions about their odour.

For the present, however, it is more important to regard the formation of these compounds from the point of view of mechanisms rather than as odorants.

It now seems well-established that the hydrocarbons, except possibly those having three or four carbon atoms, found in irradiated meats, must come mainly from the lipid. This hypothesis was previously verified in earlier studies [11], when the volatiles from irradiated methyl oleate were found to contain appreciable quantities of alkanes and alkenes, and recently in more detail from studies of both triglycerides and fatty-acid esters [12, 13].

Comparison of the volatiles produced in irradiated and oxidized butterfat has also helped understanding of the mechanisms involved [19-21]. Figure 3 shows the relative abundances of n-alkanes and n-alkanals found in a sample of butterfat irradiated at 6 Mrad, and an aliquot of the same

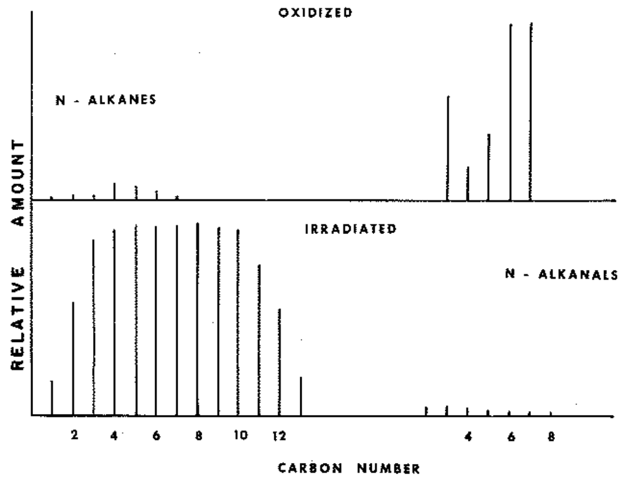


FIG. 3. Distribution of hydrocarbons and carbonyl compounds among irradiated and oxidized butter volatiles

butterfat autooxidized for one week in the presence of a copper catalyst. In accordance with the generally accepted mechanism for fat oxidation, the usual high concentration of carbonyl compounds is found in the oxidized sample. Small amounts of hydrocarbons are also found, however, probably due to the occasional recombination, or hydrogen termination, of alkyl-free radicals.

However, the presence of large amounts of hydrocarbons, and the relative lack of carbonyl compounds, even in the presence of air, shows that the mechanism for the irradiation production of volatiles is obviously different. The sensory response is likewise different. Whereas the oxidized fat is typically rancid, the irradiated fat is not, but has what has come to be recognized as a characteristic fat irradiation odour. In view of this, the attempts of many workers to correlate irradiation odour with tests, such as iodine number or TBA values, etc., are not likely to succeed.

The mechanism of irradiation damage in lipids now seems quite clear, and is relatively simple. It appears that radiation-induced, direct-bond cleavage to form primarily alkyl-free radicals can account for nearly all of the components detected upon analysis.

If, as an example, the glycerol stearate depicted in Figure 4 is considered scission of the bonds at all points of the chain with recombination or hydrogen termination of the resulting alkyl-free radicals, all the n-alkanes from methane to heptadecane could be formed. All alkanes from methane to hexadecane have been found in good yield. Moreover, if secondary collisions extracting a second electron occur, a similar homologous series of alkenes is predicted, and these also are detected in quantity. If the fatty acid were oleic or linoleic, increased quantities of olefins might be expected; and this, in fact, proves to be the case.

Study of the radiation products induced in methyl oleate, methyl stearate, trioleate and tristearin also supports the argument for a direct cleavage mechanism. Data are given in Table II and a representation of the process is given in Fig. 5. Bond cleavage would be expected to lead to an homologous series of alkanes, alkenes and esters to $C_{10}$ if the fatty

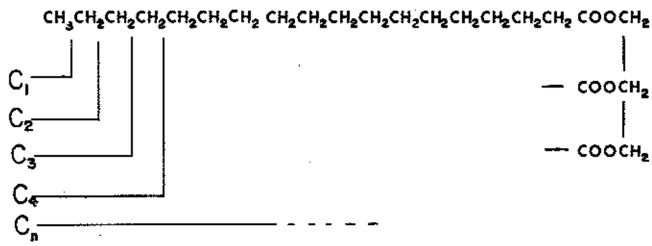


FIG. 4. Schematic diagram for proposed cleavage of alkyl groups from tristearin

TABLE II. RADIATION PRODUCTS INDUCED IN FATTY ACID ESTERS AND TRIGLYCERIDES

| | Methyl stearate | Methyl oleate | Tristearin | Triolein |
|---|---|---|---|---|
| n-alkanes | $C_1 \to C_{16}$ | $C_1 \to C_9$ | $C_1 \to C_{13}$ | $C_1 \to C_{10}$ |
| n-alkenes | $C_2 \to C_{10}$ | $C_2 \to C_{10}$ | $C_2 \to C_{10}$ | $C_2 \to C_{10}$ |
| Methyl esters | $C_2 \to C_{11}$ | $C_2 \to C_9$ | | $C_2$ only |
| | | | Acetone | Acetone |

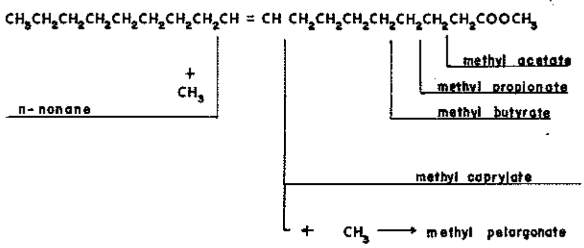


FIG. 5. Schematic diagram for proposed cleavage of alkyl and ester groups from methyl oleate

acid is oleate but would give higher homologues if the fatty acid were stearate. The principal products are, in fact, alkanes, alkenes and an homologous series of methyl esters. The highest member of the alkane series found in irradiated methyl oleate is n-nonane and the highest methyl ester is methyl pelargonate (i.e., the $C_9$ acid) whereas hexadecane is found in methyl stearate and tridecane in tristearin. No methyl esters are found, however, among the radiation products in tristearin or triolein.

Most of the other products found in irradiated meat volatiles, except those containing sulphur or aromatic rings, may also be accounted for by mechanisms associated with alkyl-free radical formation in the fat. Oxygenated compounds are far less abundant than hydrocarbons, but appreciable amounts of the members of an homologous series of n-aliphatic alcohols up to hexanol are found. Of these, only ethanol is detected in the unirradiated controls. Since the water content of meat averages nearly

60%, the formation of alcohols may be thought to occur by direct reaction of the alkyl-free radical with water. Such a mechanism is supported by the fact that only traces of alcohols are found in irradiated dry butterfat and were undetected in irradiated triglycerides or methyl esters of fatty acids.

The aldehydes and ketones are least abundant of all the compounds found which may be considered as derived from the fat. Carbonyl compounds, on the other hand, are probably produced by an indirect route which is probably similar to that involved in autooxidation of a fat. The alkyl-free radical can absorb oxygen, form a hydroperoxide, and then follow the many decomposition paths which are familiar in the oxidation chemistry of fats. The more abundant aldehydes found are unsaturated, which is in further agreement with the hypothesis that they are derived from the decomposition of hydroperoxides.

There does not seem to be much evidence that carbonyl compounds are related to irradiation odour. Chemical evidence shows them to be absent, or in low concentration, in samples which are irradiated in the absence of air, yet the irradiation odour of these samples is very definite and unmistakable. There is undoubtedly a superimposed oxidative type of rancidity which is present in meats and lipids which are irradiated in the presence of oxygen, but in oxygen-free material, uniquely radiation-induced compounds are still present. From lipids these substances are primarily only hydrocarbons.

Although minor, the contribution from steroid substances has been generally neglected. Figure 6 shows the compounds isolated from a sample of cholesterol irradiated at 6 Mrad. The principal products were a series of normal alkanes form $C_1$ to $C_7$ and a series of isoalkanes from $C_4$ to $C_8$ . The relative abundance of the iso compounds compared to the normal compounds is shown by dashed lines. The origin of these series of compounds is readily deduced to be the result of cleavage of the alkyl side chain of the cholesterol molecule.

In meats, of course, there are components which arise from the protein, which cannot be present in the products from pure fat. Table III shows some of the sulphur compounds and aromatic compounds which are also found in irradiated meats. Many of these can be postulated as arising from direct bond cleavage of amino acid moieties. Benzene and toluene may come from phenyl alanine and phenol and p-cresol from tyrosine. Recent studies have been directed to a consideration of the origin of some of the compounds from proteinaceous substances. Some of the sulphides, disulphides and mercaptans can derive directly from cysteine or methionine, but those containing more than two carbon atoms in a chain require more than a superficial explanation. To evaluate the contribution of the volatiles from the protein, as well as the lipid constituents of meat, volatile components produced in various protein substances have also been analysed.

A summary of the principal components found in haddock flesh irradiated at 6 Mrad is given in Table IV. Haddock was chosen because it was a convenient source of animal protein which is relatively fat free.

The major components identified among the volatiles produced in haddock upon irradiation are seen to be benzene and toluene, and the sulphur compounds. These compounds may be expected from the radiation-induced degradation of protein. The only carbonyl compounds found

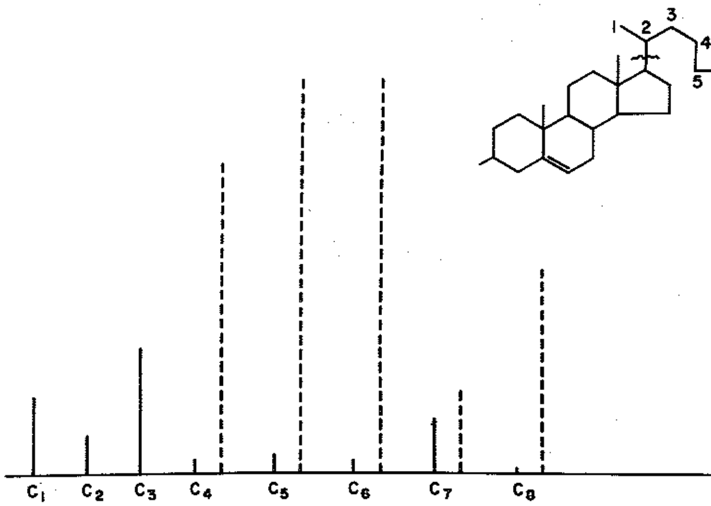


FIG. 6. Volatile irradiation products of cholesterol. Solid line - normal alkanes; dashed line - isoalkanes. Hypothetical cleavage of alkyl side chain indicated on structural diagram

are acetone and methyl ethyl ketone, and these are present in only moderate amount. Trace quantities of low molecular weight ($C_1$–$C_4$) hydrocarbons were also found. The detection of hydrocarbons, even in trace amounts, however, led to the question of whether their origin was in the protein or in the small amount of fat present in the haddock.

It thus seemed that the origin of the various components in meat volatiles could best be established by carrying out analyses of irradiation-induced compounds in meat protein and meat fat separately. Accordingly, a 500 g sample of meat, the same size sample as normally used in irradiation studies of whole meat, was separated into a protein, a lipid and a lipoprotein fraction by means of a methanol-chloroform extraction of the fat. The dry, air-free fractions were then irradiated separately with 6 Mrad gamma radiation in the same manner as that used for whole meat. The results are summarized in Table V.

The analytical results show clearly that mainly sulphur compounds and aromatic hydrocarbons are formed in the protein fraction, whereas mainly aliphatic hydrocarbons are formed from the lipid. The lipoprotein fraction produced, as expected, both aliphatic hydrocarbons and sulphur compounds. It was extremely interesting to observe that only the lipoprotein fraction had a characteristic irradiation odour.

To acquire further insight into the mechanism of the formation of these compounds, particularly of the protein-derived components, a study of the radiolysis of several amino acids was undertaken. The results of these analyses are shown in Table VI.

The major and universal product of amino-acid irradiation is carbon dioxide, which is produced in large quantities. Decarboxylation is apparently the major effect induced by the radiation. The other products, if any, are the expected decomposition products which may arise from cleavage of the side chain moieties.

Thus, hydrogen sulphide is a likely derivative of cystine and dimethyl disulphide is a likely derivative of cysteine. The formation of dimethyl

TABLE III. SOME MISCELLANEOUS COMPOUNDS IN IRRADIATED MEAT VOLATILES

| | | |
|---|---|---|
| Sulphur dioxide | Dimethyl sulphide | Benzene |
| Carbonyl sulphide | Methyl ethyl sulphide | Toluene |
| Hydrogen sulphide | Dimethyl disulphide | Phenol[a] |
| $C_1$-$C_6$ thiols | Diethyldisulphide | p-cresol[a] |
| | Methional[a] | |

[a] Radiation dose – 18 MR.

TABLE IV. VOLATILE COMPOUNDS ISOLATED FROM IRRADIATED HADDOCK FLESH[a]

| | | |
|---|---|---|
| Methane | | Methyl mercaptan |
| Propane | | Dimethyl sulphide |
| Butane | | Dimethyl disulphide |
| Butene | | |
| Benzene | | Acetone |
| Toluene | | Methyl ethyl ketone |
| | Ethanol | |

[a] Sample size – 500 g  Fat content ~ 0.3%

sulphide and dimethyl disulphide from methionine is readily deduced from expected combinations of thiomethyl and methyl-free radicals. Dimethyl disulphide is the major product.

Other amino acids were chosen to typify an aromatic, a basic, a neutral and an acidic amino acid. Of these, only phenylalanine proved to be radio-sensitive at the doses and concentration used in this study. In all the amino-acid studies, solutions or slurries of the acid were used in amounts corresponding to the average amount present in 500 g of meat, which is the usual size sample of meat. The results are in good agreement with the actual observations for meat protein, i. e., sulphur and aromatic moieties seem to be most subject to radiation cleavage.

The volatile products from the irradiation of oxytocin were examined to see if any indication of destruction of peptide bonds could be observed. The products found were mainly short chain hydrocarbons and were readily explained by cleavage of the side chains from the leucyl and isoleucyl

## TABLE V. VOLATILE COMPOUNDS ISOLATED FROM MEAT SUBSTANCES

| Protein | Lipid | Lipoprotein |
|---|---|---|
| Methyl mercaptan (l) | $C_1$-$C_{12}$ n-alkanes (l) | $C_1$-$C_{14}$ n-alkanes (l) |
| Ethyl mercaptan (s) | $C_2$-$C_{15}$ n-alkenes (l) | $C_2$-$C_{14}$ n-alkenes (l) |
| Dimethyl disulphide (m) | $C_4$-$C_8$ i-alkanes (s) | Dimethyl sulphide (s) |
| Benzene (m) | Acetone (m) | Acetone (m) |
| Toluene (m) | Methyl acetate (t) | |
| Ethylbenzene (s) | | |
| Methane (s) | | |
| Carbonyl sulphide (s) | | |
| Hydrogen sulphide (s) | | |

(l) = large; (m) = moderate; (s) = small; (t) = trace.

## TABLE VI. VOLATILE COMPOUNDS PRODUCED IN IRRADIATED AMINO ACIDS

| Amino Acid | Major Components[a] |
|---|---|
| Cysteine | Sulphur dioxide (l) |
| | Hydrogen sulphide (m) |
| Cystine | Sulphur dioxide (s) |
| | Carbonyl sulphide (m) |
| | Carbon disulphide (m) |
| | Dimethyl disulphide (t) |
| Methionine | Methyl mercaptan (s) |
| | Dimethyl sulphide (m) |
| | Dimethyl disulphide (l) |
| Phenylalanine | Toluene (l) |

[a] Carbon dioxide present in large amount in all samples.

constituents. No evidence for rupture of peptide bonds is seen. In all amino-acid and peptide radiolysis sulphur dioxide and carbonyl sulphide were found to be present in varying amounts, but at present no explanation for the formation of these compounds can be offered.

To summarize, the data thus far obtained support the simple hypothesis that radiation products are primarily the result of direct bond cleavage. The main products of irradiation of dry oxygen free lipid substances are the homologous series of n-alkanes, n-alkenes and traces of n-alkynes. Sterols give mainly normal and iso alkanes from the cleavage of the alkyl side chain. Proteins and peptides show little evidence of rupture of the peptide bond and the main products are from cleavage of the side chains on end groups. The amino acids with aromatic rings or with sulphur groups tend to be most radio-sensitive.

There is evidence that some compounds found in meat are produced by an interaction between phases. Methional, when found, is perhaps formed by interaction of a thiomethyl free radical from protein and an oxygenated free radical from the fat. Also, hexyl mercaptan or ethyl butyl disulphide would seem to come perhaps from free radicals originating in part in the protein and in part in the lipid portions of the meat. Although the current work has seemingly provided greater insight into the mechanisms of irradiation damage in meat, it has also raised more questions. Further studies will be directed toward relating the effects of irradiation on model systems of fat and protein substances in mixtures to clear up some of the questions of phase interactions.

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## DISCUSSION

E. DENTI: You have developed a remarkably sensitive analytical technique. Have you used it to study the effects of temperature (especially low temperatures) on the spectra of volatile products obtained during irradiation?

C. MERRITT: We have studied the effects of irradiation at temperatures down to that of liquid nitrogen, and find that the amount of the various components is correspondingly decreased.

E. KAMPELMACHER: You mentioned in your paper only doses of 6 Mrad. What is the lowest dose at which these odours occur?

C. MERRITT: We used other dose levels down to about 1 Mrad, and the main components were still found. We have no data for doses below 1 Mrad, so I cannot give you the threshold dose.

A. R. DESCHREIDER: Have you studied the radiolysis of an aromatic amino acid such as tryptophane?

C. MERRITT: Yes, but at the dose level and with the amount used in these experiments no product except carbon dioxide was found.

R. O. SINNHUBER: Have you attempted to reproduce the radiation flavour or odour found in irradiated lipids by preparing mixtures of the compounds characterized and subjecting them to taste panels?

C. MERRITT: We have not yet done so in a systematic manner, but this is obviously a step which must now be taken.

H. KEPPEL: Have you found that the amounts of substances estimated by you are quantitatively the same for pure solutions as for meat after irradiation, or do you believe that the energy transfer in a combination of substances, such as meat, is higher than in pure solutions?

C. MERRITT: We have no data that might serve as a basis for speculating on the relative energy transfer within the two systems.

M. INGRAM: I find it difficult to accept the suggestion that irradiation flavour is independent of the presence of oxygen. It is well known that the off-flavour is different for meat irradiated in air or in nitrogen and that, for example, different sulphur compounds are produced in the two cases. Further, if we accept that there is in either case a characteristic "irradiation note" in the off-flavours, it seems probable that, if it were due for example to alkanes or alkenes as proposed, the course of the relevant chemical changes would be influenced by oxygen. May I therefore ask how the concentration of oxygen in the system was controlled during irradiation?

C. MERRITT: One may expect to find an increased concentration of oxygenated components if the meat is irradiated in air. Nevertheless, the formation of hydrocarbon compounds is found to be independent of the presence of air, the same compounds being formed in about the same abundance whether air is present or not. The oxygen content of the flask is controlled during irradiation by removing the air under high vacuum. The final pressure in the flask is about $10^{-6}$ Torr and the oxygen content about one-fifth of that.

N. GETOFF: The behaviour of molecular oxygen under the influence of radiation is well known in principle; most of it is scavenged by the hydrogen atoms, as follows:

$$H + O_2 \rightarrow HO_2$$
$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2.$$

In addition to $H_2O_2$ formation, the $HO_2$ radicals are very reactive and act on different organic substances in the same way as the OH radicals.

G. MOCQUOT: I should like to raise a point of terminology. In your experiment on butter you say that one of the oxidized butter samples was typically rancid. A distinction is usually made between the oxidized flavour and the rancid flavour. The rancid flavour results from the liberation of short-chain fatty acids by the lipases, while the oxidized flavour results from the oxidation of long-chain, non-saturated fatty acids.

C. MERRITT: If one wished to distinguish between "rancidity" induced by microbial deterioration or by enzymes and "oxidation" odours, one would have to say, of course, that the oxidized samples had a typical "oxidation" odour. The fact remains that the odour of irradiated samples is unmistakably different and characteristic.

F. J. LEY: In view of the fact that the irradiation odours and flavours which develop in meats at certain doses are objectionable, does the knowledge of the nature of the chemical changes which occur give an indication as to how they might be prevented and the quality of the meat thereby improved?

C. MERRITT: Yes, the knowledge of chemical changes provides a great deal of information, and studies of such phenomena as the effects on these changes of dose, dose-rate, temperature, or additives to the system can yield suggestions as to how the changes may be prevented or minimized.